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***SITE-SPECIFIC MOLECULE-SURFACE
INTERACTIONS ON METAL OXIDES***

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I. SUMMARY

Collision induced dissociation of highly excited NO_2 was observed for the first time for well characterized $\text{MgO}(100)$ surfaces with parent and product angular resolution at various internal and incident translational energies, and with product NO state-selected detection. A model was developed which explains the results, and enabled comparisons with the corresponding gas-phase experiments. Scattering of $\text{HCl}(v=0)$ was examined at incident energies 0.11-0.90 eV, and demonstrated the transition between direct-inelastic scattering to trapping-desorption. At low incident energies rotational and translational temperatures of scattered HCl were equal to the surface temperature, and residence times in the millisecond regime were observed at low surface temperature. When $\text{HCl}(v=2, J=1)$ was scattered from the surface, vibrational excitation survived the process of trapping-desorption, and HCl in $v=2$ was scattered into the gas phase. The residence time, however, was less than a microsecond at all temperatures. These results were reconciled with the scattering results of HCl in $v=0$ using a model that described the competition between hopping on terrace sites, desorption, and deactivation on defect sites.

II. ACCOMPLISHMENTS

Experimental Arrangement

The experiments were carried out in a differentially pumped UHV chamber. Briefly, the scattering chamber is coupled to a differentially-pumped, pulsed nozzle source chamber where supersonic beams of reactants with well-controlled translational energies are prepared by seeding in selected carrier gases. The molecular beam is also used for He diffraction, which is a sensitive diagnostic for structural changes at the top-most surface layer, and for Xe scattering, which gives information about surface roughness. Our other diagnostics (Auger electron spectroscopy, temperature programmed desorption, time-of-flight mass spectroscopy, and REMPI) have been used by us extensively before followed. With DURIP funds, we purchased and installed high-intensity lasers (e.g., Nd:YAG laser-pumped dye lasers and narrow linewidth OPO's) which were used to efficiently prepare highly vibrationally excited molecules and detect products and reactants.

The most important experimental advance is our ability to excite molecules in molecular beams to high vibrational levels by using an "optical chopper". This is achieved by using a custom-built, high-resolution (250 MHz linewidth), tunable parametric oscillator (OPO) with active frequency stabilization. It was supplied by Dean Guyer (Laser Vision). Output of 4 mJ

at the HCl first overtone frequency was sufficient to saturate the transition. This OPO is remarkable; it enables the generation of 0.1-1 μ s beams of vibrationally excited molecules for periods exceeding 24 hrs without frequency drift.

Collision-Induced Dissociation of Highly Excited NO₂

Our work on collision-induced dissociation (CID) began a number of years ago with experimental studies of large polyatomics impinging on inert surfaces with hyperthermal incident translational energy (E_{inc}). This progressed to the inclusion of variable internal (mainly vibrational) energy (E_{int}). The independent control of E_{inc} and E_{int} has proven to be instrumental to the development of a model, described in a review article, which reconciles all of the data and also has good predictive power. For example, it has been possible to go between two regimes: (i) rebounding molecules escape the environs of the surface prior to decomposition; and (ii) the surface participates in the decomposition step. NO₂ has provided an excellent means for critically testing the model because of its large experimental and theoretical data base. Part of the motivation for these studies was the implication of excited NO₂ in the shuttle glow, which is thought to involve the recombination of NO and O. The CID experiments were difficult but worthwhile, because they provided outstanding training for the graduate students and facilitated the transition to the next experiments, which were even more sophisticated.

Inelastic scattering of HCl in $v=0$ and $v=2$ from MgO(100)

In preparation for these experiments, our laboratory underwent a qualitative upgrade: (i) a custom-built OPO for vibrationally exciting incident molecules was introduced and other lasers were upgraded; (ii) an adjacent room was annexed, increasing the size of the lab by 50%; (iii) all of the lasers were put on a single large optical table; this improved stability enormously; (iv) the UHV system was redesigned and a TOFMS was built; and (v) the HCl photoionization diagnostic was implemented. The HCl scattering experiments were carried out by using molecular beams of HCl incident on MgO(100). Surfaces were prepared such that there were minimal impurities (i.e., none that could be detected by Auger spectroscopy) and maximum crystallinity (as determined by He diffraction). This meant cleaved surfaces, heating in O₂ to fill vacancies, etc. The resulting surfaces were considered "reasonably defect free." The incident and scattered HCl molecules were monitored by using resonantly enhanced multiphoton ionization (REMPI), which is a sensitive, state-specific diagnostic.

Scattering of HCl ($v=0$, $J=0$) was examined at E_{inc} values of 0.11, 0.54 and 0.90 eV. At $E_{\text{inc}} = 0.54$ and 0.90 eV, direct-inelastic scattering occurs: the angular distribution peaks near

the specular angle; HCl rotational excitation (describable by the parameter T_{rot}) is hotter than the surface temperature (T_s); and HCl translational motion, despite considerable losses to crystal phonons, is *in no way* thermalized at T_s . Other dependencies (e.g., normal energy scaling, varying the angle of incidence (Θ_{inc}), varying T_s) are also in accord with direct-inelastic scattering. The results of this study are easily reconciled (albeit qualitatively) in terms of the direct-inelastic mechanism.

At $E_{\text{inc}} = 0.11$ eV a qualitatively different behavior was displayed. Rotational and translational excitations of scattered HCl were Boltzmann at T_s and the angular distribution was close to cosine, as expected for desorption. In addition, for T_s values ~ 150 K, a residence time in the millisecond regime was observed. Clearly, trapping-desorption is occurring at $E_{\text{inc}} = 0.11$ eV. This makes sense in light of our estimated heat of adsorption (~ 0.3 eV). This result demonstrates the transition between the direct-inelastic and trapping-desorption regimes.

Next, HCl was optically pumped to $v = 2$ prior to colliding with the surface. Initially, our thinking was that $v = 2$ excitation may promote reaction, for example yielding Cl at a Mg site and/or forming a 5-coordinated hydroxyl. However, Auger analyses (at low enough T_s values to suppress desorption) found no surface-bound Cl. At the higher E_{inc} values of 0.54 and 0.90 eV, inelastic scattering was observed, namely product translational and rotational excitations did not correspond to T_s , and the product angular distribution peaked near the specular angle. Moreover, the S/N was good considering that only molecules that survived the scattering event as $v=2$ were detected. It was our first such experiment. With modest refinements, the S/N can be increased by at least an order of magnitude. Again, this result is easily rationalized at a qualitative level. Clearly no reaction took place, maybe because the surface was too defect-free.

An exciting result was obtained when $v = 2$ was scattered at $E_{\text{inc}} = 0.11$ eV. We anticipated (based on the $v = 0$ results) that $v = 2$ would be trapped and deactivated and therefore there would be little or no signal. Maybe $v = 1$ would be produced. However, $v = 2$ was readily observed. Moreover, rotations and translations both corresponded to T_s and the angular distribution was not restricted to a lobe near the specular angle (e.g., backscattering occurs at Θ_{inc}), though it was not possible to obtain a detailed angular distribution. In other words, on the basis of all observables except HCl vibration, HCl in $v = 2$ appears to have undergone trapping-desorption. Thus, we conclude that $v = 2$ excitation has even survived a trapping-desorption process. Some $v = 1$ was detected but its concentration was well below that of $v = 2$. Clearly $v = 2$ is a major scattering channel.

Although it may seem surprising that HCl ($v = 2$) could survive on the surface long enough to reenter the gas phase, i.e. estimated residence times exceed 10 ns, the results are easily rationalized by recalling that CO physisorbed on NaCl retains its vibrational excitation for *milliseconds*. More unexpected was the observation that even though trapping-desorption was evident, the residence times were shorter than the molecular beam pulse duration (1 μ s). This was surprising, since at the same T_s HCl in $v=0$ had resides on the surface longer than a millisecond. Therefore, a model was required that would reconcile the survival of vibrational excitation in the scattered molecules, the accommodation of rotation and translation on the surface, and the short residence time of $v=2$ excitation on the surface. The model takes into account the competition between mobility on the surface (hopping), desorption, and vibrational deactivation. We assume that the trapped molecules hop randomly on the surface at a rate which depends on the activation energy for hopping from site to site on the surface. On the other hand, the desorption rate depends on the (larger) activation energy for desorption, while the vibrational deactivation rate depends on the surface phonons and surface site. In particular, flat terrace sites will exhibit a shallower physisorption wells and slower deactivation rates than defect sites (steps, corners, holes etc.). If we assume that once the molecule reaches a defect site, it never desorbs as $v=2$ onto the gas phase, we can simulate our observations by using physically reasonable values for the competing rates. Our results are also in accord with the accepted defect density on MgO(100). Developing the model took time, but we feel now confident that all the experimental observations obtained with HCl($v=0$) and HCl($v=2$) can be reconciled.

III. PERSONNEL

James Singleton — graduate student; M.A. 1997

Bruce Koel — senior collaborator, USC

Mikhail Korolik — graduate student

Don Arnold — postdoctoral fellow; left 1997 for Sandia Combustion Facility, Livermore

Matthew Johnson - postdoctoral fellow, now at Continuum, Inc.

Minda Suchan - graduate student, supported partly by a Dean Fellowship

IV. PUBLICATIONS

The effect of translational energy on collision-induced dissociation of highly excited NO₂ on MgO(100), D.W. Arnold, M. Korolik, C. Wittig and H. Reisler, Chem. Phys. Lett., **282**, 313 (1998).

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Inelastic scattering of HCl($v=2$, $J=1$) from MgO(100), M.J. Johnson, M. Korolik, D.W. Arnold, M.M. Suchan H. Reisler, and C. Wittig, manuscript in preparation.

V. PRESENTATIONS AT MEETINGS

1. "Molecule-surface collision-induced dissociation of highly excited NO₂ on MgO(100)", J. Singleton, D.W. Arnold, M. Korolik, H. Reisler and C. Wittig, ACS Meeting, Anaheim, April, 1995.
2. "Molecule-surface collision-induced dissociation of highly excited NO₂ on MgO(100)," D.W. Arnold, M. Korolik, H. Reisler and C. Wittig, 1995 Conference on the Dynamics of Molecular Collisions, Asilomar, CA, July 1995.
3. "Reactive and inelastic processes in molecule-surface interactions," D.W. Arnold, M. Korolik, M. Johnson, H. Reisler and C. Wittig, invited talk, ACS Meeting, Orlando, FL, August 1996.
4. "Inelastic scattering of HCl from MgO(100)," D.W. Arnold, M. Korolik, M.J. Johnson, H. Reisler and C. Wittig, Poster presentation, ACS Meeting, Orlando, FL, August 1996.
5. "Scattering Dynamics of HCl ($v = 0, 2$) from MgO (100)", M. Korolik, D.W. Arnold, M.J. Johnson, M. Suchan, H. Reisler and Curt Wittig, 1997 Gordon Research Conference on Chemical Reactions at Surfaces, Ventura, Feb. , 1997.
6. "Scattering of HCl ($v = 0$) from MgO (100)", M. Suchan, M. Korolik, D.W. Arnold, M.J. Johnson, H. Reisler and Curt Wittig, 1997 Gordon Research Conference on Dynamics at Surfaces, Aug., 1997
7. "Scattering of HCl ($v = 2$, $J = 1$) from MgO (100)", M. Korolik, M. Suchan, D.W. Arnold, M.J. Johnson, H. Reisler and Curt Wittig, 1997 Gordon Research Conference on Dynamics at Surfaces, Aug., 1997
8. "Scattering of HCl ($v = 0$) from MgO (100)" M. Suchan, M. Korolik, D.W. Arnold, M.J. Johnson, H. Reisler and Curt Wittig, presented by Minda Suchan at the USC Graduate Research Symposium, Catalina Island, Aug. 15-17, 1997.
9. "Scattering of HCl ($v = 2$, $J = 1$) from MgO (100)", M. Korolik, M. Suchan, D.W. Arnold, M.J. Johnson, H. Reisler and Curt Wittig, presented by Minda Suchan at the USC Graduate Research Symposium, Catalina Island, Aug. 15-17, 1997.